Electrochemical elaboration and investigation of Nitinol surfaces covered with tantalum, carbon nanotubes and phosphonic acid self-assembled monolayers

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Electrochemical elaboration and investigation of Nitinol surfaces covered with tantalum, carbon nanotubes and phosphonic acid self-assembled monolayers

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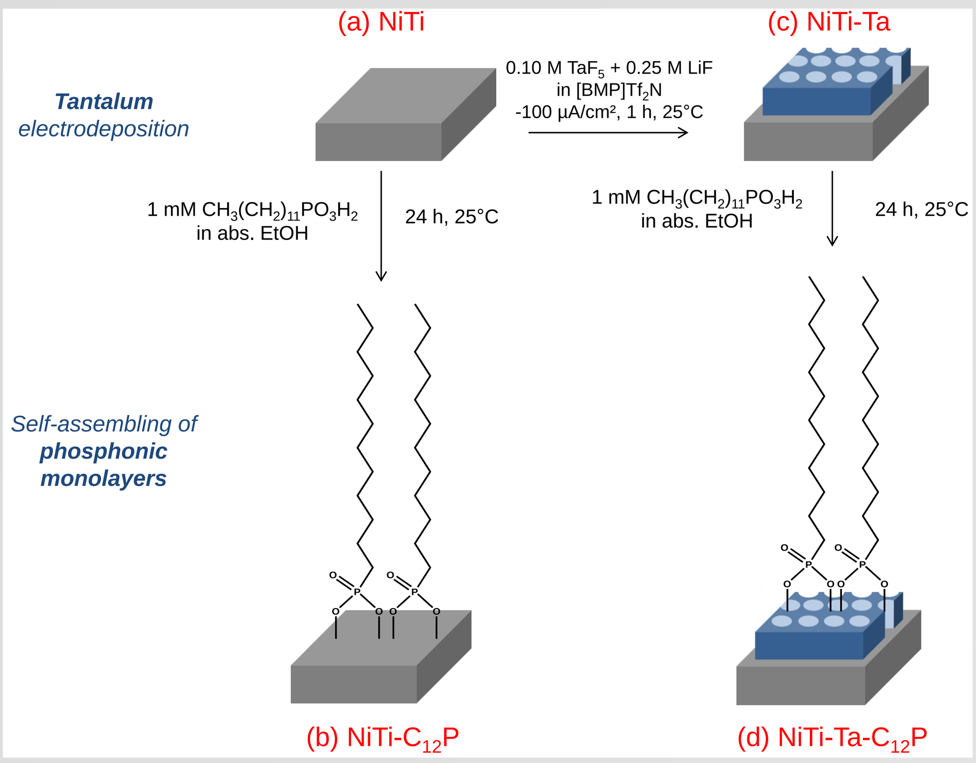
General context: **Ti-based biomaterials**

Titanium and its alloys constitute very interesting platforms for **dental and osseous biomedical applications** thanks to their low density, high fatigue strength, corrosion resistance, … More particularly, the **Nitinol** (NiTi) alloy (Ni 56%, Ti balance) is well known for its excellent shape memory and superelasticity properties. However, toxicity of certain alloying elements (Ni in NiTi, Al and V in TiAl6V4 …), long-term degradation and weak osseointegrative properties remain problematic features.

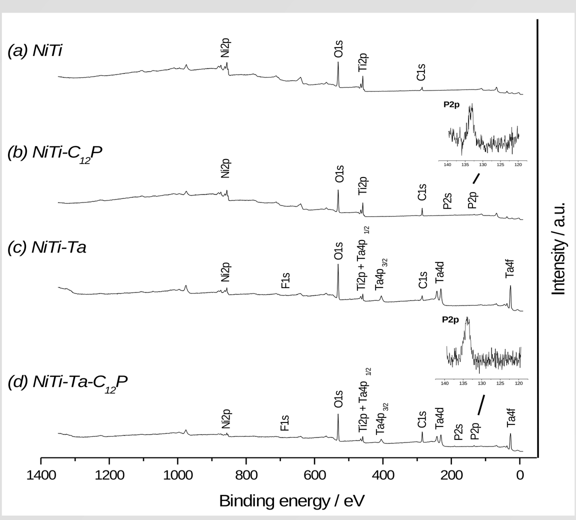
One solving approach stands in the formation of a **thin tantalum coating** on NiTi surface by an **electrodeposition (EDP)** process in **ionic liquids** media: Ta, with its very passivating oxide layer, is highly resistant to corrosion, biocompatible and bioactive, has good radio-opacity … Additional barrier effect can be brought by the further self-assembly of **alkylphosphonic acid monolayers** [1,2].

Multiwalled **carbon nanotubes (MWCNTs)** can also be incorporated to form a **composite Ta-based coating** on NiTi owing to their ability to improve the mechanical properties of the implant. They can also **specifically interact with osteoblasts and osteoclasts** and promote the bone regeneration process by **mimicking the structure of collagen fibers** and **favor the formation of an hydroxyapatite layer**. Composite Ta-CNTs layers are prepared according a **two-step electrochemical process**, first through the **electrophoretic deposition (EPD) of phosphonate-modified MWCNTs** on NiTi, than through the Ta electrodeposition on the NiTi/MWCNTs platforms [3].

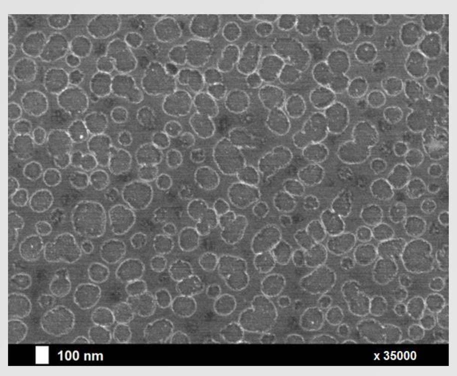
Ta electrodeposition and **alkylphosphonic acids self-assembly** on NiTi



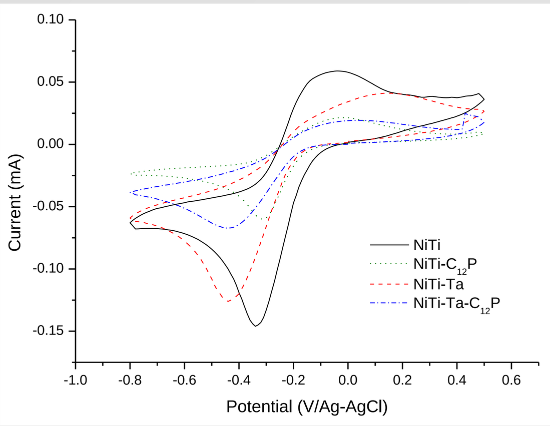
XPS – Survey



SEM
NiTi-Ta

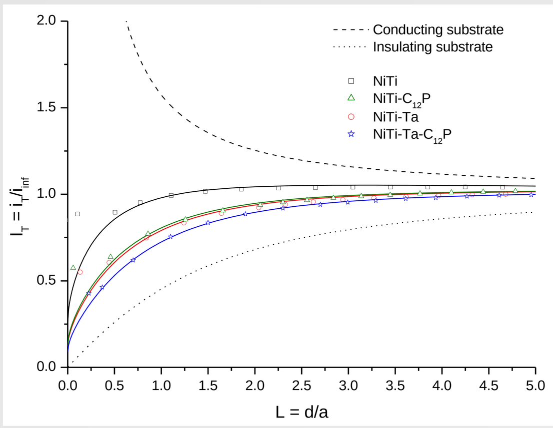


CV
Aqueous 5 mM Ru(NH$_3$)$_6$Cl$_3$ / 0.1 M K$_2$SO$_4$
v = 20 mV/s



Sample	i_p (mA)	E_p (V/Ag-AgCl)	$k_{app}°$ (10^{-4} cm/s)	k_{eff} (10^{-3} cm/s)
NiTi	-0.146	-0.34	3.1	4.6
NiTi-C_{12}P	-0.060	-0.31	2.9	1.9
NiTi-Ta	-0.126	-0.45	0.92	1.7
NiTi-Ta-C_{12}P	-0.067	-0.44	0.87	1.1

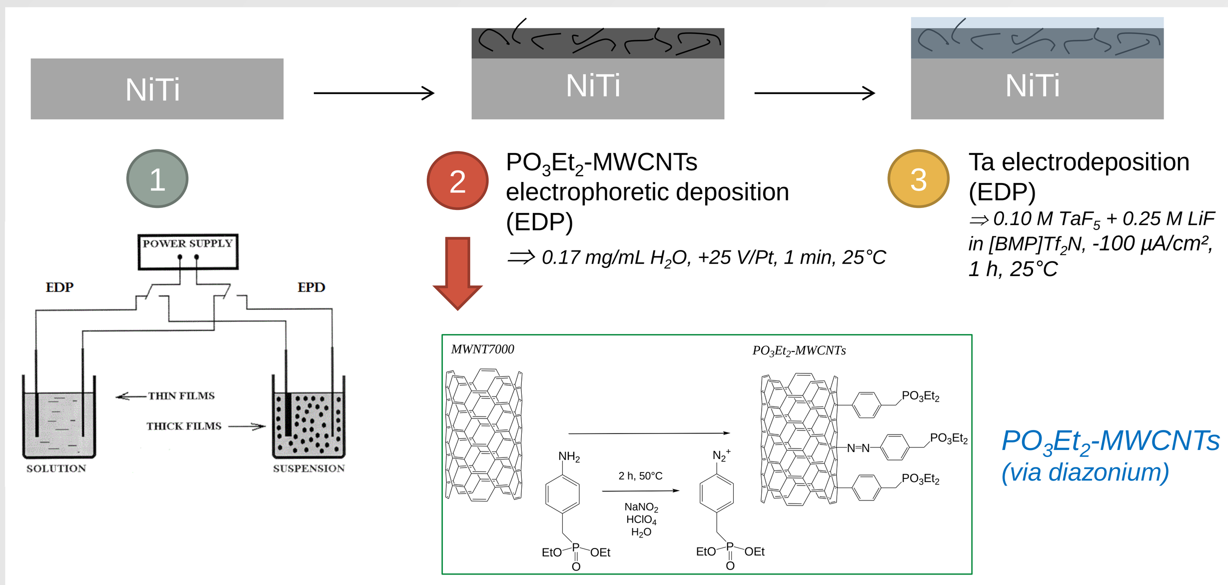
SECM – FB PAC
Aqueous 5 mM Ru(NH$_3$)$_6$Cl$_3$ / 0.1 M K$_2$SO$_4$
E_{tip} = -0.70 V/Ag-AgCl; $E_{substrate}$ = OCP



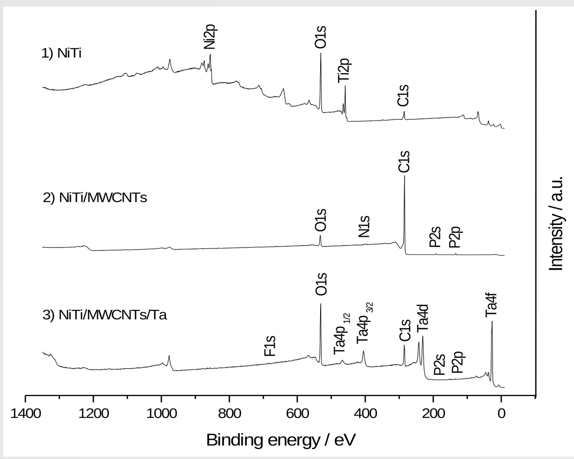
- **Electrodeposition of a spontaneously nanostructured Ta film** on NiTi (« microscopic » pores; ϕ ~120 nm).
- **Self-assembly of C_{12}P monolayers** on NiTi and NiTi-Ta with surface covering ratios of 68 and 41%, resp. (« macroscopic » defects).

  ⇒ Specific electrochemical responses on CV and SECM curves.

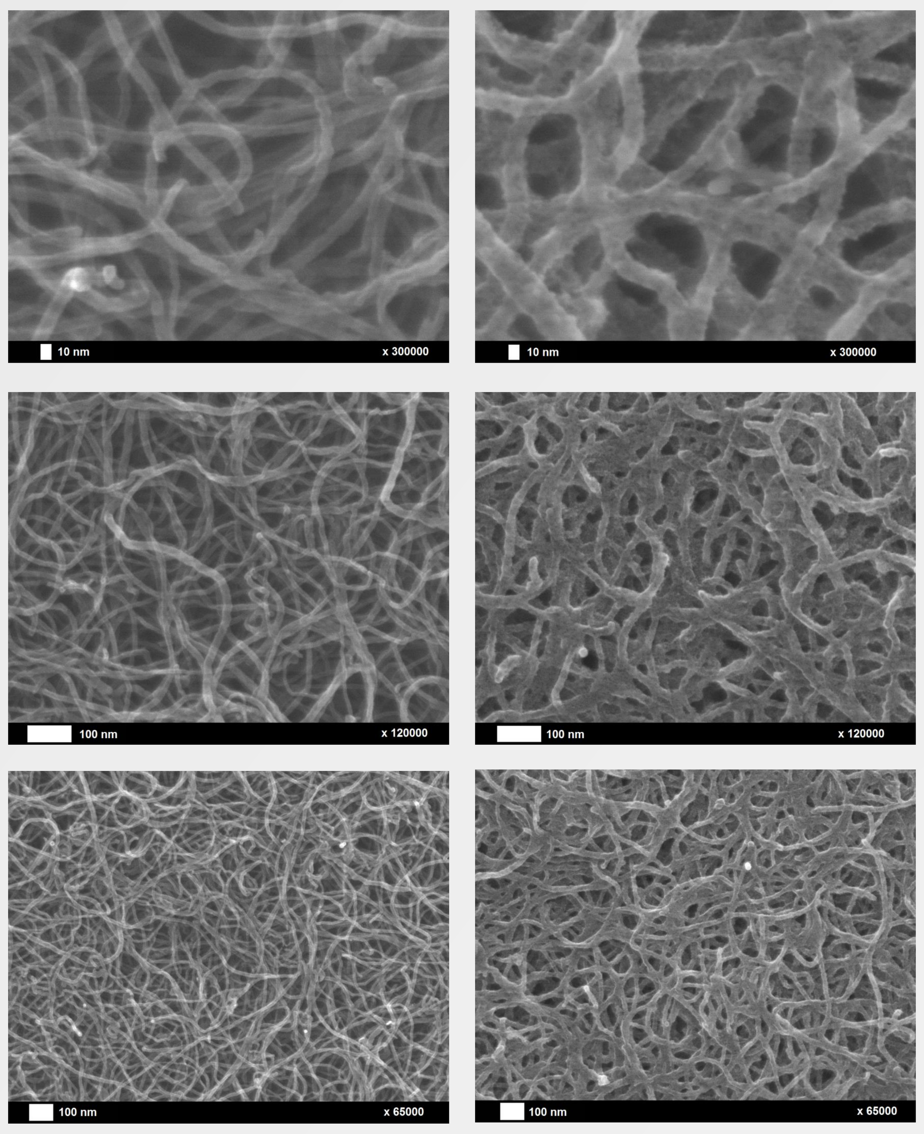
MWCNTs electrophoretic deposition and **Ta electrodeposition** on NiTi



XPS – Survey

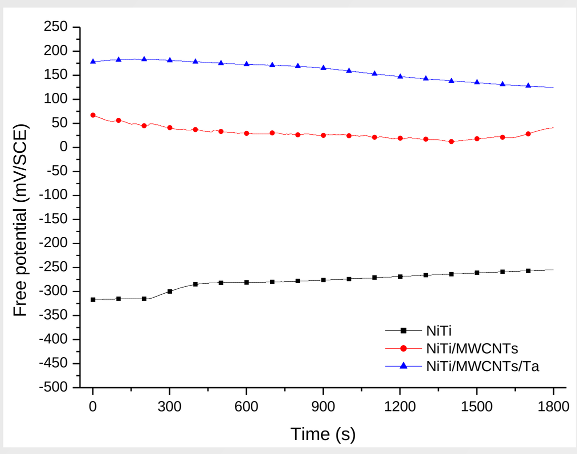


SEM

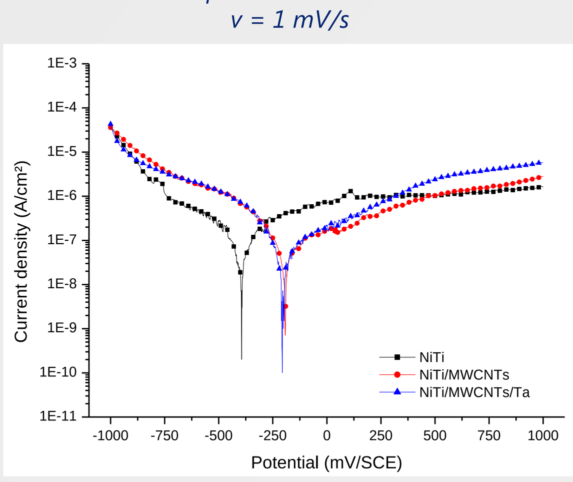


NiTi/MWCNTs *NiTi/MWCNTs/Ta*

Free potential
Aqueous NaCl 0.9%



LSV
Aqueous NaCl 0.9%
v = 1 mV/s



The **electrochemical co-deposition of PO$_3$Et$_2$-MWCNTs and Ta on NiTi** lead to the generation of **compact, homogeneous and functional composite layers presenting strong barrier properties** at the interface with the external environment.

Conclusions and perspectives

- Electrochemistry is used for **both elaboration and characterization of protective and functional surface coatings on Nitinol substrates** with a high level of versatility and precision.

- The considered approaches lead to **highly homogeneous, nanostructured and adherent tantalum-based layers**.

- Such **organic-inorganic hybrid films** are therefore strongly believed to constitute **sensitive platforms for further osseointegrative purposes** (nucleation of hydroxyapatite, adhesion-proliferation of osteoblasts and osteoclasts).

References

[1] A. Maho, J. Delhalle, Z. Mekhalif, Study of the formation process and the characteristics of tantalum layers electrodeposited on Nitinol plates in the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid, *Electrochim. Acta* 89 (**2013**) 346-358.

[2] A. Maho, F. Kanoufi, C. Combellas, J. Delhalle, Z. Mekhalif, Electrochemical Investigation of Nitinol/Tantalum Hybrid Surfaces Modified by Alkylphosphonic Self-Assembled Monolayers, *Electrochim. Acta* 116 (**2014**) 78-88.

[3] A. Maho, S. Detriche, G. Fonder, J. Delhalle, Z. Mekhalif, Electrochemical Co-Deposition of Phosphonate-Modified Carbon Nanotubes and Tantalum on Nitinol, *ChemElectroChem* (**2014**) in press.

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